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Nanoparticle-Seeding Approach to Buried (Semi) Metal Film Growth

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Final Report

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Final Report: Nanoparticle-Seeding Approach to Buried (Semi)Metal Film Growth (Grant FA9550-12-1-0404)

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Abstract

We explored an entirely new growth mode for epitaxially-integrating (semi)metallic films with high-quality III-V semiconductors, which could be particularly important to the future of multi-modal sensors, specifically vertically-integrating a diversity of sensing modes onto a single “pixel.” In such devices, it is highly desirable that electrical contact can be made independently to each detector in the pixel stack for electrical readout – requiring transparent, epitaxially-compatible, electrical conductors. ErAs and many of the other rare-earth monpnictides (generally denoted as RE-V) are rocksalt semimetals that can be grown epitaxially on zinc-blende III-V substrates, with thermodynamically stable interfaces. However, the rotational symmetry mismatch between the III-V and ErAs results in a high density of planar defects in III-V layers grown on ErAs, akin to the challenges associated with GaAs growth on silicon. To circumvent this limit, we employed a seed layer of buried ErAs nanostructures. ErAs layer growth then proceeds sub-surface, with a GaAs capping layer floating above. The advantage of this technique is that the GaAs capping layer remains registered to the underlying substrate, preventing planar defect formation during subsequent III-V growth. We concentrated on two important directions: (1) identifying the relevant growth conditions necessary for growing thicker layers and (2) characterizing the electrical/optical properties most germane to integration into devices.

Regarding (1), thicker layers are of great interest for buried Ohmic contacts to minimize series resistances, and were our focus. To this end, we increased the maximum thickness of an ErAs film by 4x and have developed a model for understanding the key challenge, which should enable us to further increase the achievable thickness. We have also grown an ErAs/GaAs composite structure of 14.5 nm total ErAs thickness, which is ~10x the thickness we achieved before the program’s inception.

Regarding (2), our efforts focused primarily on the electrical properties of the ErAs nanoparticle-seeded film and the luminescence efficiency of the III-V grown above the nanoparticle-seeded film. Both are essential for future device integration. We found that the resistivity of nanoparticle-seeded films exhibit a negative temperature coefficient (i.e. increased conductivity at low temperature) confirming that band-like transport is the dominant conduction mechanism, consistent with that expected for a continuous metal layer. This confirms that the nanoparticle-seeded film growth method succeeds in accessing a new lateral conduction regime for ErAs structures embedded in GaAs without formation of planar-defects in the GaAs overgrowth, at least to within the sensitivity of our transmission electron microscopy (TEM) studies. To gauge the optical properties of the overgrown III-V, we employed an InGaAs quantum well (QW) grown above a nanoparticle-seeded film as a sensitive probe of the optical quality. Though we observed a ~20x reduction in luminescence efficiency compared with an otherwise identical ErAs-free control, the luminescence efficiency was improved by >300x when compared to conventional ErAs film growth. Moreover, the InGaAs QW grown on the conventionally-grown ErAs film control was entirely optically dead. This finding is very encouraging for future device applications, though more effort is warranted to further improve the optical quality of the overgrown III-V.

1. Overview of Growth Method

In the embedded film growth method, sketched in **Figure 1**, the ErAs layer growth proceeds sub-surface, with a GaAs capping layer floating on top. This capping layer remains registered to the underlying substrate, preventing planar defect formation during subsequent III-V growth. The benefits are clearly observed in the TEM images shown in **Figure 2**, where planar defect formation is strongly inhibited with even a 1 nm GaAs capping layer.

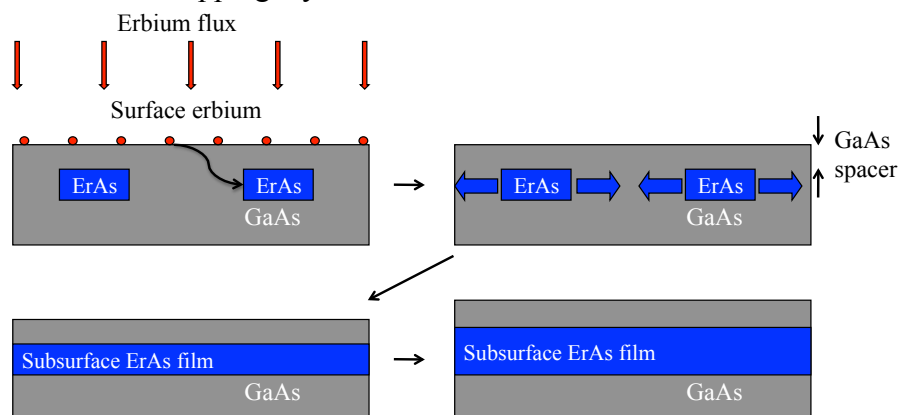


Figure 1. Schematic of the film growth process employing a layer of buried ErAs nanostructures as a seed for film growth. The surface GaAs capping (spacer) layer ‘floats’ on the ErAs film and remains registered to the underlying GaAs substrate, preventing planar defect formation during subsequent III-V growth.

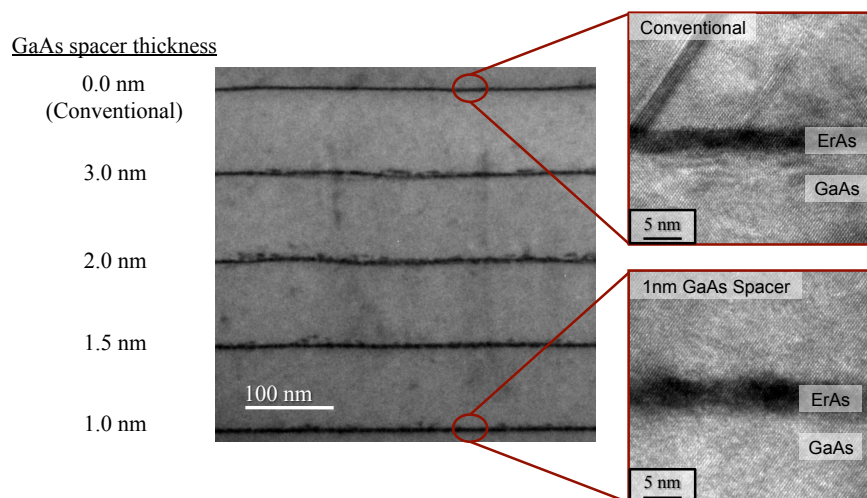


Figure 2. Transmission electron microscopy (TEM) image of five monolayer thick ErAs films, grown using various GaAs spacer thicknesses. Insets: High-resolution TEM images. Note that planar defect formation has been inhibited using a 1 nm GaAs spacer, as compared with the layer grown by the conventional growth technique (0 nm spacer).

2. Towards Nanoparticle-Seeded Growth of Thicker Films

Our initial efforts focused on the growth of thicker layers using our initial growth conditions. **Figure 3** shows *in situ* reflection high-energy electron diffraction (RHEED) pattern after 5 and 20 monolayers (ML) of ErAs deposition. Note the significant degradation with increasing deposition, in terms of (1) spotting of the diffraction pattern, (2) dimming and loss of higher order diffraction features, and (3) severe chevroning, indicative of roughness and faceting. In order to better understand the

critical growth parameters for this film growth technique, we sought to develop a model for erbium incorporation, shown schematically in **Figure 4**.

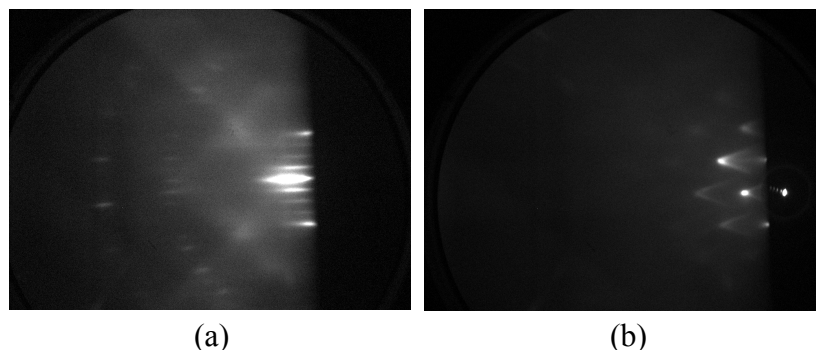


Figure 3. Reflection high-energy electron diffraction (RHEED) images of the embedded film growth process after (a) 5 monolayers (ML) and (b) 20 ML of ErAs growth. Note the significant degradation of the surface morphology after 20 ML.

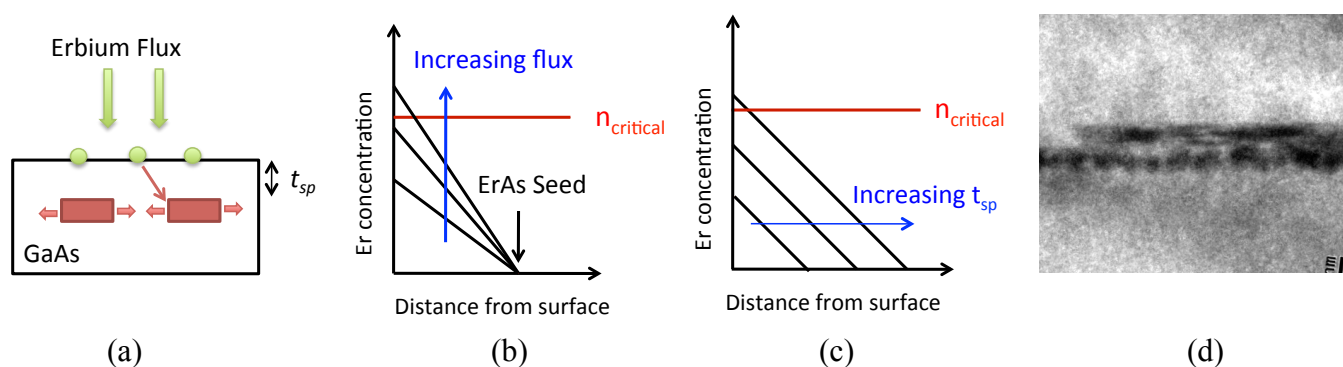


Figure 4. Model for erbium incorporation during embedded film growth, which is equivalent to the minority carrier distribution in a short base transistor. (a) Cross-sectional sketch of embedding process, (b) erbium surface concentration versus distance from the surface, which is pinned at zero at the ErAs seed particles, and (c) the role of increasing the spacer thickness, t_{sp} . It is essential to avoid building up sufficient surface erbium concentration to seed the formation of ErAs nanoparticles on the surface. (d) Indeed, formation of a second layer of nanoparticles is evident in transmission electron microscopy (TEM) of embedded films using our initial growth process.

Because there are no volatile ErAs compounds at the growth temperature, we can use a simple diffusion model with the only source of erbium at the surface and the only sink at the subsurface ErAs nanoparticles. The model is then analogous to the minority carrier concentration in a short-base bipolar-junction transistor, where the slope of the erbium concentration corresponds to the flux (or growth rate). The steady state surface concentration is a function of the erbium growth rate and the GaAs spacer thickness. The critical surface erbium density for the formation of a second nanoparticle layer, $n_{critical}$, limits the growth rate that can be successfully employed for a given GaAs spacer thickness. Indeed, too high of an erbium deposition rate results in the formation of a second layer of nanoparticles, seen clearly in the transmission electron microscopy (TEM) image in **Figure 4d**.

By reducing the erbium flux during embedded growth, we were able to inhibit the formation of a second layer of nanoparticles, shown in **Figure 5**, even for significantly higher levels of ErAs film deposition. We were able to grow layers as thick as 20 ML, $\sim 4x$ thicker than previously achieved, albeit with somewhat degraded morphology. Additionally, the composite thickness of ErAs in the multilayer structure shown in **Figure 5** is 50 ML, $\sim 10x$ thicker than our previous best result.

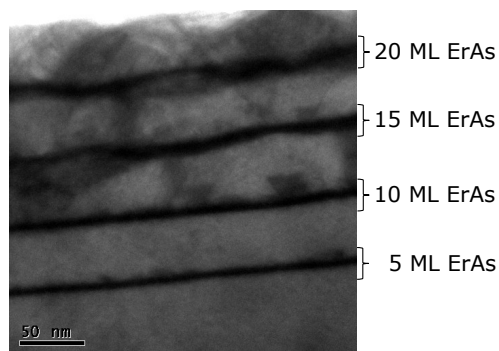


Figure 5. Cross-section TEM image of a multilayer ErAs (dark) / GaAs (light) structure, with single layer thickness as high as 20 ML, $\sim 4x$ thicker than our best initial result, albeit with degraded morphology.

3. Electrical Properties of Nanoparticle-Seeded Films

Figure 6 shows the temperature-dependent conductivity of 5 and 10 ML ErAs films, from room-temperature to 77 K. The negative temperature coefficient (i.e. increased conductivity at low temperature) confirms that band-like transport is the dominant current mechanism. This confirms that the nanoparticle-seeded film growth method succeeds in accessing a new lateral conduction regime for ErAs structures embedded in GaAs without formation of planar-defects in the GaAs overgrowth.

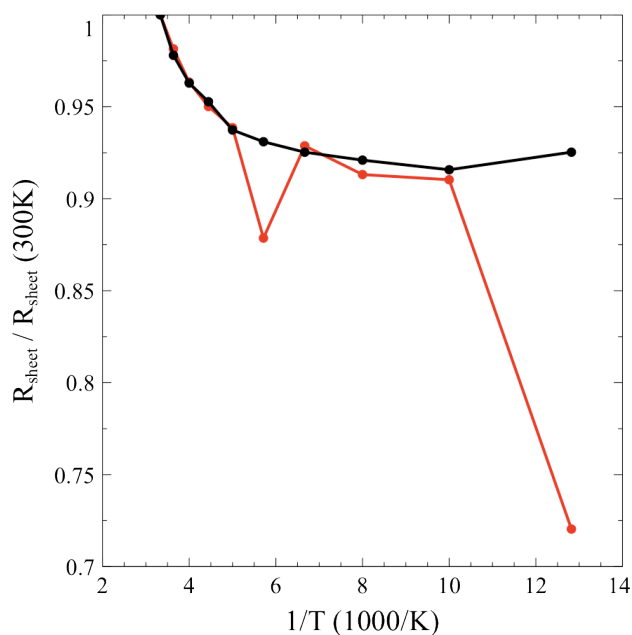


Figure 6. Temperature-dependent conductivity for 5 and 10 ML ErAs films, grown with the nanoparticle-seeded film growth method. Conductivity, normalized to room-temperature conductivity, was extracted from transmission line measurements. The weak temperature dependence indicates band-like transport, consistent with electron transport in a continuous conductor, rather than the hopping-type conduction exhibited by overgrown ErAs islands.

4. Optical Properties of III-V Materials Grown Above Nanoparticle-Seeded Films

While previous measurements of thin ErAs films exhibited defect-free overgrowth, the optical quality of the overgrowth will be paramount for devices to leverage the ability to embed metallic films.

For 5-10 ML thick ErAs films, TEM measurements indicated suppression of planar defects, however, defect densities well below the detection limit of cross-sectional TEM can have dramatic effects on device performance. To more sensitively characterize the quality of the III-V grown above a nanoparticle-seeded film, we employed the photoluminescence (PL) structures sketched in **Figure 7**, to quantify the effects of embedding ErAs films below optically active regions. The PL structure consisted of an InGaAs QW, emitting at 960 nm, embedded in a 200 nm GaAs absorbing region and surrounded by AlAs carrier blocking layers. The carrier blocking layers prevented photogenerated carriers from recombining at the surface or underlying epitaxial layers. As such, this structure is particularly sensitive to nonradiative recombination within the PL structure. Because of the strong dependence of carrier lifetime on parasitic erbium incorporation, care must be taken to remove parasitic erbium flux and sink surface erbium concentration prior to the growth of the PL structures. For the structure shown in **Figure 7a**, the ErAs film was used to sink surface erbium.

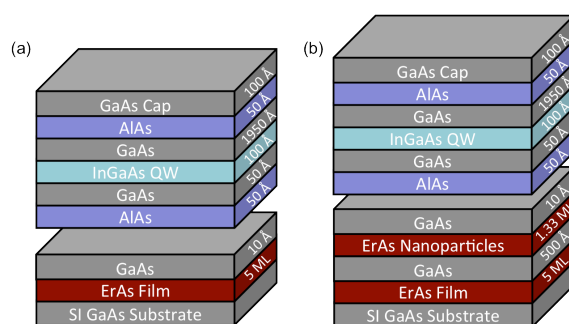


Figure 7. Photoluminescence test structures used to quantify optical quality of overgrowth of ErAs films: (a) structure utilizing ErAs film to sink parasitic erbium and (b) structure utilizing a second ErAs nanoparticle layer to sink parasitic erbium.

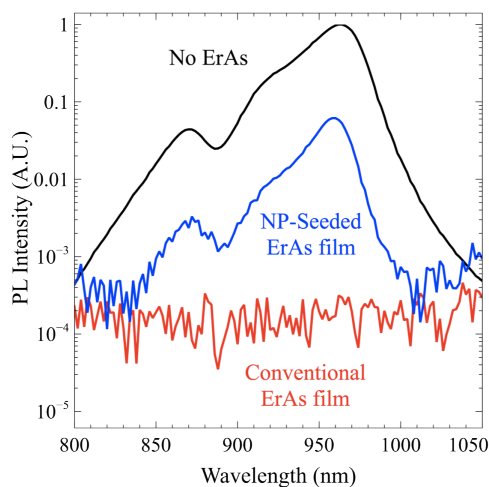


Figure 8. Photoluminescence spectra from an ErAs-free control sample, a sample containing a conventionally grown 5 ML ErAs film, and a sample containing a 5 ML ErAs film grown with nanoparticle-seeded film growth method. Luminescence from the conventionally grown film was undetectable as it was below the noise floor. Note the >300x improvement in luminescence efficiency using the nanoparticle-seeded growth technique.

Figure 8 shows the room-temperature photoluminescence spectra for 5 ML ErAs films, one grown conventionally (**red**) and one grown with the nanoparticle-seeded film growth method (**blue**), as

well as an ErAs-free control sample (black). The spectra from the conventional ErAs film corresponded to the noise in the system as the lock-in amplifier was unable to lock onto any emission. The lack of any discernable emission indicates the poor quality of the overgrowth of conventional ErAs films, consistent with the TEM studies summarized in **Figure 2**. However, the peak PL intensity for the nanoparticle-seeded ErAs film (NP-seeded ErAs film) was only $\sim 20\times$ lower than the control sample. While this result is promising for devices requiring embedded ErAs films, the origin of the degradation is not clear and more study is warranted.

Careful erbium management was required to prevent parasitic erbium incorporation into the PL structure, a high temperature anneal was introduced with only 1 nm spacer between the surface and the embedded ErAs film. In order to determine if the degradation is intrinsic to the overgrowth of the film or an artifact of this anneal, PL measurements on the structure from **Figure 7b** were conducted. The structure introduced a separate nanoparticle layer to sink the surface erbium prior to growth of the PL structure, allowing for overgrowth of the ErAs film without a growth interruption. This structure allowed the ErAs film to be embedded in a manner identical to those used for the TEM investigations. Because we previously showed that the use of nanoparticles to achieve a surface suitable for high optical quality overgrowth has previously been demonstrated, any degradation in optical quality is believed to be attributable to defects generated in the overgrowth of the nanoparticle-seeded ErAs film. The PL spectra for the samples with the nanoparticle layer and that without were nearly identical indicating that the degradation in the optical quality is intrinsic to incorporating the ErAs film. Even so, the PL signal was $\sim 100\times$ stronger than samples with 10^{15} cm^{-3} parasitic erbium doping and would likely be of sufficient quality for use in several electrical devices. Additionally, the PL measurement gives a high sensitivity to defect formation that can be used to refine the growth method and improve the overgrowth quality.